Deterioration of recent oak by iron compounds - a comparison with *Vasa* oak

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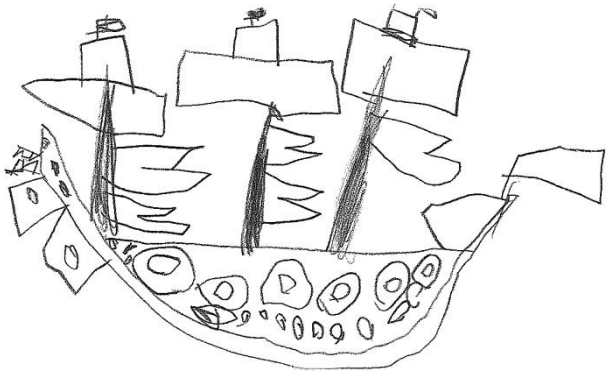

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The cover image is the view of the *Vasa* by my six years old son
Sebastian Norbakhsh

Deterioration of Recent oak by Iron compounds - a Comparison with *Vasa* oak

Abstract

Wood degradation in the historical warship *Vasa* has been studied systematically regarding the chemical and physical properties. The presence of iron(II) seems to be one important factor for the degradation of the wood, causing reduction of its tensile strength. This is unfortunately a serious problem as iron(II) compounds are abundant in *Vasa* wood. However, it is a question whether the deterioration reactions still go on or if they have stopped soon after the ship was salvaged. The aim of this study is to investigate the possible chemical reasons for the deterioration of the wood. This has been accomplished by use of model experiments with recent oak. Series of recent oak wood, cut in a "dog bone shape", were placed in aqueous solutions containing 0.1 M iron(II) chloride. These samples were exposed to different concentrations of oxygen for one week, one month and one year. By use of an Instron universal testing machine the samples were pulled apart and the tensile strength required to break the wood registered. Samples exposed to iron(II) and oxygen showed a significant decrease in tensile strength. Variation of time and oxygen exposure showed that the rate of decrease in tensile strength is more intense at the initial stages of the exposure. The results also showed that exposure to pure oxygen, increased the deterioration rate. Oxygen treated samples showed an increase in the formation of low-molecular organic acids in the wood tissue and pH decreased to approximately 2 to 3. The chemical properties of holocellulose in recent oak treated with aqueous iron(II) solutions in the presence of oxygen conforms very well with degraded wood from the *Vasa*. The deterioration process in the *Vasa* wood seems to be limited in time and probably took place soon after oxygen exposure. The abundance of iron(II) compounds in *Vasa* wood and accessibility of oxygen and water will determine the level of deterioration of the wood.

Keywords: The historical warship *Vasa*; iron; oak wood; tensile strength; oxalic acid, acid hydrolysis, oxidative degradation.

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Dedication

To my son, SEBASTIAN, without him I would never reach so far.

Better a diamond with a flaw than a pebble without.

Confucius (551 – 479 BC)

Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text

I Johansson, C; Bjurhager, I and Almkvist, G. A study on the mechanical properties and degradation of oak wood. Effects of iron(II) and oxygen on the mechanical strength in the longitudinal direction. (Manuscript)

II Johansson, C; Bjurhager, I and Almkvist, G. A study on the mechanical properties and degradation of oak wood. Oxygen consumption related to iron initiated degradation of recent oak wood. (Manuscript)

Abbreviations

AMW	Average molecular weight
EDS	Electron-dispersive spectroscopy
EMC	Equilibrium moisture content
EPA	Environmental protection agency
EPR	Electron paramagnetic resonance
ICP-AES	Inductively Coupled Plasma- Atomic Emission Spectrometry
IEC	Ion exchange chromatography
Mol Wt	Molecular weight
PEG	Polyethylene glycol
RH	Relative humidity
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
TS	Tensile strength

1 Introduction

1.1 History

This is the story of a great achievement which crashes in disappointment and death, and about war, conquest and politics. In the 17th century, Sweden became one of the strongest and most fearful countries in Northern Europe. By the crowning of king Gustavus II Adolphus in 1611, an exceptional strategist and skilled politician was coming to power. During his rule a three fronted war was a fact and he managed to conquer almost the whole Scandinavia, parts of Russia, Poland and Germany and make Sweden to a Northern European empire. However, these wars were disastrous to domestic politics and people suffered in poverty, diseases and lack of labor as almost half of the population (the majority of the male population) was fighting in the frontlines of these wars. To keep the empire intact, one of the most strategically important tasks was to control the Baltic Sea around and within (Glete, 2006). During the 1620th the Swedish fleet was afflicted with a series of unfortunate backlashes, e.g. in the storm at the coast of Riga (1625) and the battle of Danzig (1627). The king was of course aware of this and ordered five extensively large warships of its time of which the major one was the *Vasa*. The history does not end here. On the contrary, it begins in 1628 after two years of intense ship building the *Vasa* was ready for its maiden voyage into the seas. The scene was certainly glorious and spectacular for the spectators but it didn't last for long, it shattered to trepidation and consternation. On August 10, 1628 the *Vasa* set sail from the port of the island "*Gamla stan*" in Stockholm. After approximately a nautical mile at sea nearby the small island of Beckholmen a gust of wind caused the ship out of control and she heeled over and water poured into the ship through the open lower gun ports. She sank standing within minutes to the bottom of Stockholm

harbor with only the masts sticking out of the water. The engineer Anders Franzén located the wreck of the *Vasa* in 1956, and in 1961, after nearly 333 years on the bottom of Stockholm harbor, she saw the sunlight again.

1.2 Public view

The first impression when people enter the Vasa museum is a kind of "WOW-feeling" because of the impressive size and the way the *Vasa* is presented. The ship itself is unique in the sense of preservation and completeness. The *Vasa* offers a combination of science and history in one package and shows when engineering is failing at its best. Hopefully the *Vasa* will stand for generations to come as she is not only a piece of Swedish history, she stands in the front of new discoveries of archeological marine waterlogged wood artifacts in the world.

1.3 Scientific view

The 333 years on the seabed with low temperature and fairly dirty brackish water in the Stockholm harbor kept this amazing piece of history in good shape. The major reactions and natural degradations were inhibited much because of an anoxic and toxic environment with high concentrations of hydrogen sulfide and the low temperature in the Baltic Sea, +1 to +5 ^{o}C (Barkman and Franzen, 1972), during the time at the seabed (Sandström et al., 2002). Almost immediately after the disaster nearly all the bolts, cannon balls and objects made of iron began to corrode. Due to locally high concentrations of dissolved iron a penetration of iron(II) ions into the wood was inevitable (Håfors, 1990, Almkvist and Persson, 2006). Iron can now be found everywhere in the ship timbers and on the surfaces, in various amounts and depths (Fors and Sandström, 2006, Almkvist and Persson, 2008a). The chemical properties of iron(II) and iron(III) will play a significant role in the chemistry and preservation process of the *Vasa* which will be discussed later in this thesis. During this time a considerable amount of waste was dumped in Stockholm harbor (Fors, 2008). The almost anaerobic conditions with reduced microbial degradation were beneficial to the wood. At the same time the near anoxic conditions favored the sulfur reducing bacteria which reduce sulfate to hydrogen sulfide, H_2S (Sandström et al., 2002). It must be stressed that the microbial activity and the deterioration of the surface wood during the time on the seabed was slow and executed by fungi and

to some extent by erosion bacteria which are the primary degraders of wood at low oxygen conditions (Björdal and Nilsson, 2002).

The problem with erosion bacteria in the wet wood of the *Vasa* was a concern when the ship was salvaged. To deal with this problem, considerable amounts of boric acid/borax 1-4 % were mixed with the chosen conservation agent polyethylene glycol (PEG) (Håfors, 2010, Fors, 2008). PEG is a hygroscopic substance with high viscosity. The purpose of PEG was mainly to replace the water within and beside the wood cells to act as a dimensional stabilizing agent (Håfors, 1990). By introducing PEG the problem of shrinkage and cracking of the wood, especially in areas where pressure and curvatures are more common, were prevented. After almost 20 years of spraying with aqueous solutions of PEG on the surface of the ship, analyses showed that the PEG diffusion into the *Vasa* wood was restricted to a few centimeters from surface. It is also shown that PEG is primarily spread in the rays in radial direction of the wood. However, the tensile strength in the longitudinal direction of wood is moderately/none affected by PEG impregnation (Bjurhager et al., 2010). Compression tests on *Vasa* wood and recent oak wood without any modifications showed that the radial modulus and compressive strength of the *Vasa* oak wood is 50% lower than that of recent oak (Ljungdahl and Berglund, 2007) and some observations of *Vasa's* keel, which is resting on logs, shows a deformation of the keel due to the high pressure from the weight of the ship.

Figure 1. Deformation of the *Vasa* keel, reshaped by the weight of the ship. The pressure on the radial direction has passed the yield point and probably will be permanently damaged. (Photo: Swedish National Maritime Museum)

The *Vasa*, like any other man-made structure, consists of curvatures and bent parts which induce a local tension inside the timbers. The curvature is often parallel to the longitudinal direction, and if the condition of the wood micro structure inside the timber is in bad shape, the wood will eventually burst. To prevent this scenario, tests of tensile strength in the longitudinal direction is momentous.

Figure 2. Elucidates the curvature on the port side of the *Vasa* (Photo: Swedish National Maritime Museum).

1.4 Wood chemistry

Wood at the macro-scale could be described as a composite material consisting of different plant cells oriented in such a way that their functionality is fulfilled. Wood is divided in two major categories, i.e. hardwood and softwood. These two types vary in the sense that the ratio of abundance of the cells and their functionality, shape and chemical composition is different. Hardwood and softwood are also further divided into two important sub-groups, called heartwood and sapwood. Heartwood contains only of dead cells and constitutes the part around the pith which is the center of the trunk. The color has a darker tone than sapwood due to higher content of extractives. The primary objective of heartwood is as support tissue. Sapwood is a mix of dead and living cells and it is located at the outer part of the trunk. Its color is lighter than heartwood and serves for the water transport from the roots to other parts of the tree. A three-dimensional view of craved section of a wood trunk is divided into a longitudinal, radial and tangential direction (Figure 3).

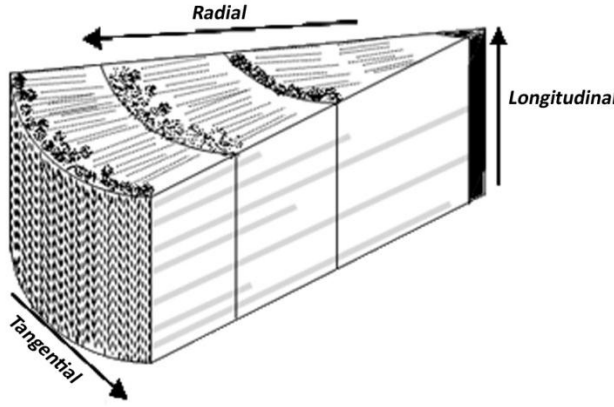

Figure 3. Macro-scale image of a piece of wood trunk. It shows the radial, tangential and longitudinal directions (Daniel, 2009, Bjurhager, 2011).

The radial direction rays of cells, ray-parenchyma, are dominating. These are living cells with thin cell walls allowing liquids to pass between cells. This kind of cells constitutes 90-95% of the softwood, while hardwood comprises 7-30% of the total wood volume as radial wood cells (Daniel, 2009). On the other hand, in hardwood the dominating types of cells are the longitudinal parenchyma. The cells are elongated and called vessels. Hardwood consists of smaller and more compact cells, fibres. Together with vessels they form the base of hardwood. The size difference between late- and early fibre cells is small and that is why the annual rings in hardwood are not as pronounced as in softwood. In most cases the cell wall structure consists of three main layers. The first and third layer (S1 and S3, respectively) are thin and the cellulose micro-fibril chains are oriented horizontally, while the middle layer (S2) is much thicker and the orientation of cellulose chains is almost vertical relative to the fiber axis (Figure 4).

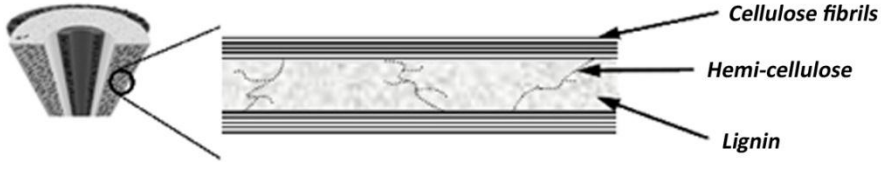

Figure 4. An image of a plant cell wall with primary, secondary and tertiary layers. The direction of micro-fibrils of cellulose is clearly shown and a magnification in the secondary wall (S2) displays the three major components; Cellulose, Hemicellulose and Lignin (Henriksson, 2009, Almkvist, 2008).

The main component of the fibres is cellulose which is a straight polymer chain with repeating sequences of D-anhydroglucopyranose residues. The residues are joined together with 1 to 4 ß-glycosidic bonds without any side chains (Figure 5). The degree of polymerization of cellulose is very high and due to this fact plants rely their mechanical stability on the cellulose structure.

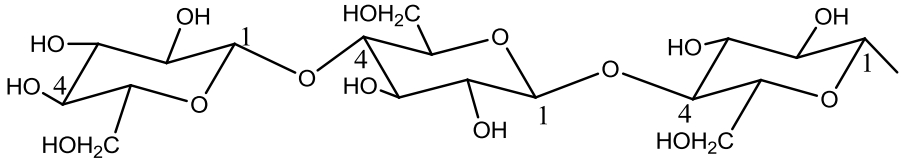

Figure 5. Cellulose chain with three D-glucose rings connected by 1-4 ß-glycosidic bonds.

Other components present in the cell wall are hemicelluloses and lignin. Hemicellulose differs from cellulose in the sense that the polymer chain is built of several different sub-residues. The polymer chains are not straight as in cellulose and there are many side chains branched to the longer main chain. The degree of polymerization is much lower than in cellulose, and hemicelluloses are often/always imbedded in the irregular polymer named lignin. Hemicellulose acts as a connection chain between the fibrils while the plant cell grows.

Lignin in wood acts as a kind of filling material. It is a hydrophobic non-linear and irregular polymer. Lignin makes the wood more firm and water-repellant. It is believed that this attribute works as a defense mechanism for plant cells. The chemistry of lignin is complex but can be described as polymerization of aromatic compounds connected to each other by ether and carbon-carbon bonds (Holmgren, 2008). The main repeatable sub-molecules for lignin are *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The relative amounts of these three monolignols depend on the type of plant. The type of lignin in hardwood is dominated by the sinapyl alcohol monomer while it is almost absent in softwood tissue, where instead the dominating monomer is coniferyl alcohol (Henriksson, 2009).

Wood extractives are the non-structural components in wood tissue (Hillis, 1971), limited to a few percent of the total mass of wood. The extractives are rather easy to separate from the wood with different solvents, thereby the name. They have a low degree of polymerization compared to lignin and cellulose. There are a variety of different

extractives with alternating abundances with respect to location and type of plant. Extractives are more abundant in heartwood where the dead cells are dominating compared to sapwood. There are extractives with different properties regarding hydrophilic properties and easiness of separation by aqueous solutions, while those with more hydrophobic features such as fatty acids, sterols, terpenes and waxes are rather easily dissolved in low polarity organic solvents (Jansson; et al., 2009).

1.5 Polyethylene glycol

Polyethylene glycol (PEG) is a linear polyether chain synthesized from aromatic ethylene oxide in alkaline solution. The repeated unit in the polymer chain is $(CH_2CH_2O)_n$ terminated by alcohol groups in both ends. The number of ethylene oxide units, n, determines the average molecular mass of PEG (Figure 6), e.g. PEG 600 has approximately 13 $(CH_2CH_2O)_n$ units. The solubility of PEG in both organic solvents and aqueous solutions (Roberts et al., 2002) makes this polymer suitable for a wide range of applications. The chain lengths determine the physical properties, as state of aggregation, viscosity and melting point. Longer polymer chains of PEG ($\sim M_w \geq 1000$) have a waxy character while shorter chains are highly viscous liquids at room temperature. Chemically, PEG with different chain lengths have many features in common. For instance, PEG is amphiphilic and can dissolve in organic solvents as well as aqueous solutions, as the polymer properties derive from the ether oxygens and the terminal alcohol groups (Håfors, 2010). In conservation methodology the reversibility of treatments of artifacts is important. PEG is one such substance which is easy to work with, non-toxic and reversible.

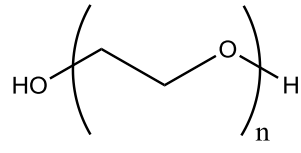

Figure 6. The back bone of polyethylene glycol showing the terminal sites and the repeatable ethylene oxide unit.

After the salvation of the *Vasa* in 1961 the risk of cracks and shrinkage of the waterlogged wood depended on the evaporation of water inside the wood. To avoid this to happen, it was decided that the ship and the loose objects should be impregnated with a chemical substance which would fill the water-filled wood cells emptied on cellulose and to support

and stabilize the structure on a micro scale level. The chemical and physical properties of PEG settle the choice of preservation medium. Aqueous solutions of PEG with different lengths, mainly PEG 1500, 600, in that order, were sprayed on the surface of the ship during approximately two decades. At the end of PEG treatment PEG 4000 was introduced by hand on some of the surfaces of the upper decks. Later studies showed that the penetration of PEG has not been as sufficient as expected (Håfors, 2010). PEG was found at all depths of degraded wood, while low or no PEG had diffused into sound wood (Mortensen et al., 2007).

1.6 Iron chemistry

The chemistry of iron is a vast and almost infinite subject to describe. Historically iron has been used by man for nearly 6000 years. It is the fourth most abundant element in the earth crust and occurs in its most oxidized state as the mineral hematite (Fe_2O_3). Other common iron minerals are magnetite (Fe_3O_4) and pyrite (FeS_2), where the latter is mainly used in industry for its sulfur content (Earnshaw and Greenwood, 1997).

Corrosion of iron has always been a topic related with iron chemistry. It is described and defined as an electrochemical process which involves electron transport toward an oxidizing agent from metallic iron. These reaction mechanisms are known as redox reactions. This means that iron increases its oxidation number by 2 or 3 units (occasionally higher) depending on the number of electrons lost and the chemical conditions. This process occurs when oxygen, water and an electrolyte are present.

1.7 Present work

Previous studies of tensile strength of the wood of *Vasa* has shown a significant weakening in strength in the longitudinal direction compared to recent oak (Bjurhager, 2008). This is even more pronounced in deeper parts of the wood. *Vasa* like any other structure has many parts with curvature and these are parallel to the fibers in the longitudinal direction. Thereby, strength in the longitudinal direction of the wood is important for the stability and steadiness thus *Vasa* stand on its own weight in the museum hall.

Size exclusion chromatography of the *Vasa* wood secondary cell walls has shown that the degree of polymerization of holocellulose has

decreased extensively compared to recent oak (Lindfors et al., 2008). Almkvist et al. (2008a) showed that significant concentration of soluble hemicelluloses, mainly 4-O-methyl-glycurono-xylan, diffused out from *Vasa* wood when treated with water. Moreover, a decrease of average molecular weight of PEG was observed (Almkvist and Persson, 2008a).

One of the suggestions on what kind of processes is causing these changes of physical and chemical properties may in fact be the high amount of iron in the wood of *Vasa*. Generally, deterioration of wood by iron compounds is described in many previous studies (Bawn, 1953, Scott, 1965, Uri, 1956). It is also suggested that iron in the presence of oxygen in a Fenton-type reaction could generate hydroxyl radicals ($^{\bullet}OH$). Hydroxyl radicals are highly reactive and they can react with all organic substances (Halliwell and Gutteridge, 1992, Hammel et al., 2002). It is established that the presence of iron compounds has a deteriorating effect on polysaccharides in wood (Browning and Bublitz, 1953, Emery and Schroede.Ha, 1974).

Previous studies have concluded that iron in the *Vasa* wood originates mainly from corroded iron objects during the time on the seabed and was mainly accumulated as hydrated iron(II) ions inside the timber, and as iron(II) sufides and pyrite, FeS_2, and rust in the surface region (Fors and Sandström, 2006). The first discovered abnormality signs were salt precipitations on the surface of the polyethylene glycol treated wood of *Vasa* which indicated that chemical reactions are ongoing or have taken place inside the wood. Scanning electron microscopy-Energy Dispersive Spectroscopy (SEM-EDS) analyses have shown the distribution of iron in the wood. Iron seems to accumulate specifically in the lumen and within the cell walls (Almkvist and Persson, 2011). According to Almkvist et al. extended X-ray Absorption Fine Structure (EXAFS) measurements of samples from the *Vasa* at different depths of the wood showed that the mean Fe-O bond distance in the iron compounds present at larger depths of the *Vasa* wood is about 2.06 Å, showing that iron is mainly present in the oxidation state +II (Almkvist and Persson, 2011). Decreasing mean Fe-O bond distances show an increasing content of iron(III). Iron(III) compounds are dominating in the immediate surface. It must also be stressed that in deeper parts of the wood the pH is lower due to significant amounts of low molecular acids as acetic, formic, glycolic and especially oxalic acid.

One of the suggestions, as mentioned above, is a Fenton type reaction which takes place when iron (Fe^{2+}), oxygen (O_2) and hydrogen peroxide (H_2O_2) react in an acidic aqueous environment forming hydroxyl radicals ($^{\bullet}OH$). Although no H_2O_2 has been detected in *Vasa* wood it is suggested that Fe^{2+} (aq) and O_2 (g) in the presence of oxalic acid could generate enough peroxide for a Fenton reaction to occur (Hyde and Wood, 1997). Oxalic acid ($pK_{a,\,1}$ = 1.23) is one of the main low molecular acids formed deep into the wood of the *Vasa*, and in the areas with severe chemical degradation, rather high concentrations have been found (Almkvist and Persson, 2008a). Iron(II) oxalate may cause an auto-oxidation reaction with oxygen to produce superoxide and thereby the peroxide needed for the formation of hydroxyl radicals (Hyde and Wood, 1997).

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\bullet-} \qquad (1)$$

$$Fe^{2+} + O_2^{\bullet-} + 2\,H^{+} \rightarrow Fe^{3+} + H_2O_2 \qquad (2)$$

The hydrogen peroxide will react with Fe^{2+} to produce $^{\bullet}OH$ and the Fenton reaction mechanism is complete.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \qquad (3)$$

The time dependence of the presence of oxygen is one of the main factors which will answer the question whether the degradation of the wood components such as holocellulose or lignin is ongoing today, or if it did stop soon after the ship was salvaged.

In addition to the low pK_a value of oxalic acid, there is a study claiming that oxalic acid may play an important role in the reduction of iron(III) to iron(II) (Schmidt, 1981). However, this suggestion is controversial and has been rejected by S. M. Hyde and P. M. Wood (1997), who claimed that the reduction of iron(III) is rather caused by a photolytic conversion than by spontaneous decomposition as mentioned by Schmidt (1981).

The deterioration of wood is more pronounced where the iron concentrations are relatively high while the concentration of sulfur is low (Almkvist, 2008). The question was whether an iron catalyzed reaction causing the deterioration of wood by the generation of free radicals could be inhibited by sulfur compounds, and if so, how effective would it be?

Cysteine is an amino acid with a thiol as a side functional group. The sulfur in cysteine acts as a free radical scavenger and can inactivate the

powerful oxidation ability of the free radicals (Harman et al., 1984, Darkwa et al., 1998, Meister and Anderson, 1983). Cysteine was used as an antioxidant in our model studies in order to mimic the abundant amount of reduced organic sulfur species in the wood of *Vasa* (Almkvist and Persson, 2011, Almkvist and Persson, 2008a, Fors, 2008).

Deeper parts of timber have been more or less protected from the surroundings and the diffusion of polyethylene glycol into the wood has been limited. It can therefore be assumed that the condition of the wood deep into large beams is more or less unchanged compared to when the ship was on the seabed. Iron(II) is the dominating form of iron at larger depths of the *Vasa* wood (Almkvist and Persson, 2011). This indicates that the accessibility of oxygen has been limited. However, the question remains, when oxygen, in sufficient concentrations, reaches these regions, how fast will these reactions be and how much may iron(II) compounds induce or catalyze the reactions causing a reduction of the mechanical strength of wood? Moreover, how is tensile strength affected by the presence or absence of wood extractives, and will lack of extractives slow down or speed up these reactions?

The objective of this study was to understand the chemical effects of iron(II) on recent oak (*Quercus robur*) wood regarding change in mechanical properties and generation of low molecular acids in the presence of oxygen, polyethylene glycol and reduced sulfur compounds. Much of this information can be extended to the present situation for the *Vasa* wood and thereby a view of the deterioration reactions taken place and when they possibly occurred.

2 Material and Methods

2.1 Sample preparation

2.1.1 Solid samples

The wood chosen for this study originated from a tree trunk of European oak, *Quercus robur*. The plank was bought from a commercial carpentry workshop in Stockholm. The plank was a part of heartwood and it had normal annual ring widths, free of knots and seemingly without infestations and/or degradation by fungi. First, the wood was cut into five sections in tangential direction (A, B, C, D and E). Each of these smaller pieces was again divided further into four arbitrary sections in longitudinal direction, such that each piece followed the annual rings. This was of great importance because the micro-fibril angles (MFA) increase toward the bark direction (Lichtenegger et al., 1999, Barnett and Bonham, 2004) which should cause that the samples would not been uniform in tensile strength testing. The plank had a small rotation through it regarding the annual rings, which was solved by cutting the wood in the same rotational direction, so that both sides of the samples contained the same annual ring (Figure7).

These pieces were sawn into three smaller sections, and at last the samples could be carved out. The final cut resulted in “dog bone” shape samples with dimensions in the midsection of 2 X 4 X 100 mm in tangential, radial and in longitudinal direction, respectively. At the edge parts for the grip the radial part increased successively to 15 mm and 50 mm added in longitudinal at each side. The overall length became 200 mm.

Figure 7. A schematic image of dog bone shape sample preparation. The enlarged part is the actual picture of the transverse section showing marks and annual rings.

2.1.2 Impregnation

The samples chosen for different treatments were pair cut out next to each other and one of them was used as a reference. The references followed the same treatment as the samples but without any iron(II) treatment. The samples were divided into different groups depending on the type of treatment and the time of exposure to oxygen. Moreover, three groups were treated further with cysteine, PEG and acetate. The references of these three groups were treated with iron(II) chloride. This was complimentary to investigate a third chemical. The samples were soaked in 0.1 M iron(II) chloride in aqueous solution prepared from 99% $FeCl_2 \cdot 4H_2O$ (Sigma Aldrich). The deionized water used was degassed by bubbling nitrogen gas immediately before preparation of the solutions. To discard the gases, especially oxygen, inside the cavities of the wood and to reach a better impregnation of iron in the wood, the samples were subjected to low pressure. The pressure was decreased to ca 200 mbar. The chamber was filled up with nitrogen gas. This was repeated 5 times before the iron solution was changed once more, and the procedure was repeated. The samples were left in the oxygen free glove box for 10 days for drying.

The iron(II) solutions were discarded. Some of the treatment groups were left in the glove box during the dying period, while the rest were exposed directly to oxygen in wet condition. The concentration of oxygen was 21 and 100 volume percent. Before tensile strength testing the samples were weighted until the difference during 24 hours did not exceed 0.1 %. The samples required approximately 10 to 20 days until they reached equilibrium in a relative humidity of 55% at atmospheric pressure and ambient room temperature. Equilibrium moisture content (EMC) of wood was measured by weighing before and after drying of samples. The samples kept in RH 55% contained 10-12% water. This is in agreement with values reported previously (Simpson, 1998). No significant difference

in EMC between samples and references could be seen. EMC regarding samples treated in 98% RH shows a moisture content of about 40%. A significant difference between samples and references were observed. Wood samples treated with iron(II) chloride solution have generally a slightly higher moisture content despite that equilibrium regarding weight loss is reached.

One group of samples was pre-treated with different solvents in order to separate the extractives. This group would monitor the action of iron when extractives are absent. In a first step the wooden samples were soaked in a mixture of acetone/water with a fraction of 7:3, followed by a mixture of toluene/ethanol (2:1) for ten days. The samples were dried another ten days waiting for complete evaporation of the solvents. After this treatment the wooden samples became pale and odorless. The samples were then impregnated with iron(II) chloride as described above.

Three groups were treated differently from previous groups in order to investigate other reactions caused by iron in particular. One group of samples were impregnated with 30% (w/v) PEG 600 (Aldrich) mixed in deionized water after the impregnation with iron(II) chloride. Another group were pre-treated with 0.1 M of 97 % L-cysteine (Aldrich) before the treatment with iron(II). A third group was treated in acetate/acetic buffer at pH 4 before iron was introduced. The corresponding references to these three groups of samples were impregnated with iron(II) chloride.

All the sample and reference groups except for one were exposed to either 21 or 100 percent oxygen for a time of one week, one month and one year, respectively.

2.2 Powder samples

2.2.1 Extractions

Wood chips of oak were milled and sieved to 250 µm (mesh 60). In order to lower the amount of wood extractives a series of extraction steps was performed by use of a Soxhlet apparatus. The wood powder was rinsed with a solution of acetone/water (7:3 v/v) for 12 h and air-dried for 24h (Lindfors et al., 2008). The second step was further Soxhlet extracted with toluene/ethanol (2:1 v/v) for another 9 h and air-dried for 48 h. The last step was performed with a mixture of 2-propanol (anhydrous 99.5%) and 1% sodium hydroxide. pH-indicator paper showed a pH around 9 for this

solvent. The wood powder was washed for an additional 5 h. The residual powder was carefully rinsed with water and pH was adjusted with an acetic/acetate buffer to approximately pH 4. After every step the residual solvent was checked by use of iron(III) chloride salt to ensure the separation of the extractives. The complex formation reaction between iron(III) and tannins was obvious and the immediate change of color to dark purple indicates successful separation.

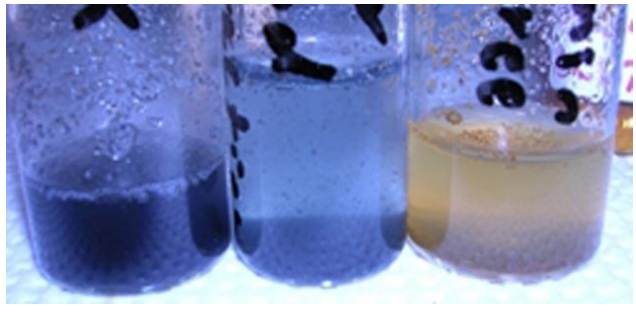

Figure 8. Loose of tannins show a discoloration of the solution containing iron(II) chloride. The darkest (left) is oak powder without any extraction. In the middle the sample was treated with acetone/water (7:3 v/v) and toluene/ethanol (2:1 v/v). Almost no blackish color was seen after the treatment with 2-propanol and 1% sodium hydroxide.

2.2.2 Impregnation of wood powder

Collected aliquots were placed in vials. A solution of iron(II) chloride was prepared as described above and added to the sample vials in an oxygen free environment. The reference sample was also prepared from untreated oak powder, and treated with the same solutions. The samples were soaked and shaken time to time during 48 h. The samples were filtered and rinsed several times with degassed water. 55% relative humidity prevailed during drying. To keep the same relative humidity in the reaction vials a smaller sized vial (climate conditioning vial) was placed inside. Dried powders were then poured into measuring vial beside the conditioning vial.

2.3 Analyses

2.3.1 pH

To measure pH, the wood samples were ground to pieces to a size of around 0.5-1 mm in diameter. Approximately 100 mg of the ground

sample was soaked in deionized water for two days. The samples were sonicated 3-4 times each day. pH was measured with a micro combination electrode (Hamilton Spintrode) immersed into the unfiltered solution.

2.3.2 Tensile tension testing

The strength of the wood was measured by use of an Instron universal testing machine 5566 with a lastcell of 10 kN and a rate of 1.0 mm/min. The tests were performed at a relative humidity (RH) of 53% and a temperature of 23 °C. The specimen and dimension loading force at fracture were used for calculation of tensile strength. Prior to every mechanical testing, the sample was measured with a digital vernier caliper and marked with a white Tipp-ex on the midsection. Two dots with 90 mm between made the instrumentation's video extensometer register and measured the differentiation (strain) between the marked distances. These measurements were performed at the department of Fiber and Polymer Technology, Royal Institute of Technology.

2.3.3 IEC (Ion-Exchange Chromatography)

The content of low molecular organic acid and sulfate in the samples was determined by use of a Dionex (ICS 2000) ion chromatograph assembled with a Dionex AS 15 column (4X250 mm) which is applied to measure inorganic anions and organic acids such as acetic, glycolic, formic and oxalic. Solutions were prepared as described in the pH section above but this time the wood was filtered off. The aqueous samples were injected and eluted with 35 mM of potassium hydroxide at a rate of 1.2 ml/min. The characterization was obtained by comparing the retention times of the peaks to the retention of its references with same substance. The integration of the obtained peaks gave the quantitative information. The samples were analyzed by Innventia AB in Stockholm.

2.3.4 SEC (Size-Exclusion Chromatography)

Size exclusion chromatography, SEC, is a separation technique based on the distribution of different substances in a sample into the porous structure of the immobile stationary phase. It is a retention method using different size and/or mass of substances in the sample. Smaller molecules have higher retention than larger ones due to their ability to diffuse through the porous material of the stationary phase in the column (Poole and Poole, 1991). This technique has been applied in the *Vasa* project to

measure the degradation of holocellulose in wood from *Vasa* and recent oak (Lindfors et al., 2008). The analyses were performed by Innventia AB in Stockholm.

2.3.5 ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometry)

ICP technology was utilized for qualitative and quantitative analysis of total content of elements. Equipped with a flame, (plasma) which produces a temperature of nearly 10,000 °C (Harris, 1998), this technique is able to ionize all the elements in the periodic table. For the total concentration of iron and sulfur, dry wood samples were sent to an authorized laboratory, ALS, Luleå. The analyses are measured according to EPA 200.7 and 200.8 standards.

2.4 Oxygen measurements

The relative oxygen pressure in the headspace of the airtight sample vial was regularly measured by use of a Fibox3 sensor (PreSens Precision Sensing GmbH, www.presens.de), which uses photoluminescence technology. This technology is utilized to measure oxygen pressure *in situ* or in incubated samples (Matthiesen and Wonsyld, 2010).

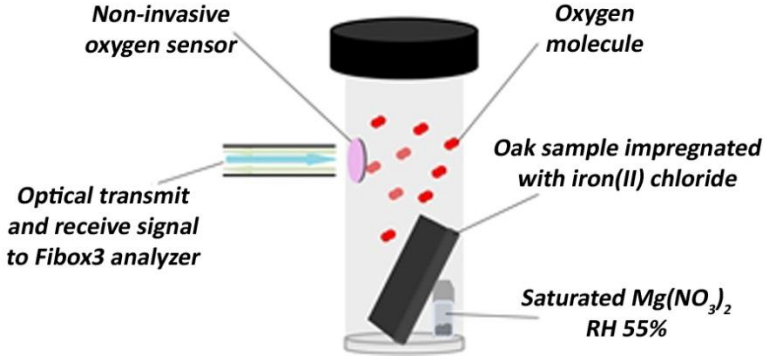

Figure 9. Schematic description of the oxygen monitoring experiments. The sensor attached inside the glass vial is excited and due to the concentration of oxygen the emitted radiation is measured and converted.

Oak wood specimens from the same trunk of wood as used for tensile strength measurements with the sizes 42 mm in longitudinal, 12 mm in radial and 2 mm in tangential directions were impregnated with 0.1 M iron(II) chloride. The iron solution was prepared as described above. The

treated samples were dried in an oxygen free environment. A smaller vial containing saturated magnesium nitrate solution was placed inside the reaction tube to give a RH of 55%. The samples were placed into the reaction vials and exposed to air oxygen until equilibrium was reached. The samples were then incubated. The concentration of oxygen in the atmosphere of the vials was monitored daily by the "*Presens Fibox 3 minisensor oxygen meter*". A silicon rubber compound (RS 692-542) glue was used to assemble the oxygen sensors inside the reaction vials before insertion of the samples. This makes it possible to measure the oxygen concentration in the headspace.

3 Results and discussion

3.1 Iron diffusion into the wood

The impregnation efficiency was tested at a preliminary stage at different levels of iron(II) chloride concentrations, Figure 10. An impregnation solution of 0.1 M resulted in an iron content in the wood at roughly the same level as found in the inner parts of the *Vasa* wood suffering from chemical degradation (Almkvist and Persson, 2008a). This concentration was also the one used (0.1 M) in all other experiments involving impregnation of oak wood.

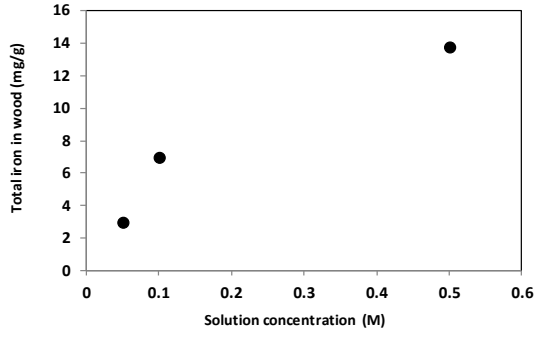

Figure 10. Total iron concentration in wood as a function of treatment concentration with iron(II) chloride.

The total concentration of iron in the midsection of the samples treated with iron(II), cysteine and PEG 600 is shown in Table 1. The total concentration of iron in samples treated by 0.1 M iron(II) chloride solution is around 5–6 mg/g. The concentration of iron declines to approximately 3 mg/g for the core of the samples. The order of treatment does not influence the concentration in the core while a decline for the whole piece

is observed. The measurements for samples treated with cysteine followed by iron(II) resulted a molar ratio of Fe:S at 0.8. The results from treated “dog bones” gave an Fe:S ratio of 1.9.

Table *1*. Total concentration of iron and sulfur for the midsection of “dog bone” shape samples. Core part of samples treated with iron(II) chloride and cysteine in different order.

		$Fe_{(mg/g)}$	$S_{(mg/g)}$
midsection	$FeCl_2$ (aq)	5.27	0.08
	$FeCl_2$ (aq)-->PEG_{600}	3.71	0.07
	Cysteine-->$FeCl_2$ (aq)	4.89	1.44
	Solvent-treated + $FeCl_2$ (aq)	4.50	0.07
Inner	$FeCl_2$ (aq)	3.10	0.10
	Cysteine-->$FeCl_2$ (aq)	2.93	2.10

In the case of PEG treatment, the solution of PEG is more viscous and the diffusion of iron solution into the wood became much slower and therefore the treatment with PEG was performed after the treatment with iron. This is preferable as it resembles the process used for the *Vasa*.

Scanning Electron Microscopy-Energy Dispersive Spectroscopy, (SEM-EDS), analysis of the impregnated samples showed that iron(II) ions had penetrated into the wood matrix leaving only minor parts with low or non-detectable levels of iron. As a complement, ordinary photos were taken of the cross-section showing that dark and light areas corresponding to areas with high and low iron content, respectively. The parts of the wood matrix that turned out to be harder to impregnate applied specifically to the rays which could be seen as white stripes in the surface, indicating the lack of iron in these wood elements (Figure 11).

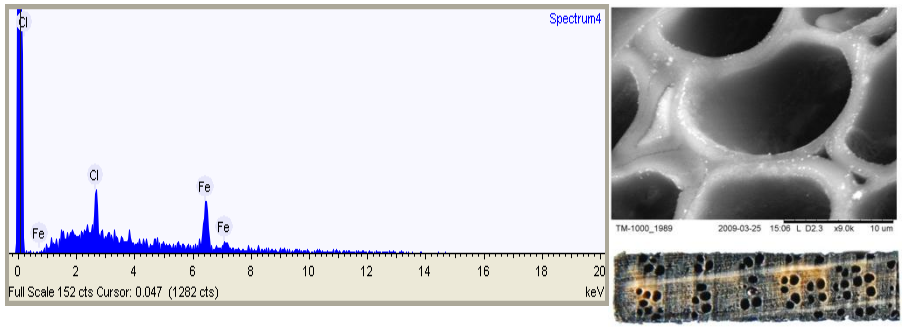

Figure 11. SEM-EDS analysis shows clearly iron and chloride peaks from the lighter dots accumulated on the cell-walls (left). SEM-image (upper right) X9000 and photo of a cross-section from a sample impregnated with iron(II) chloride (lower right). Note the darker and lighter areas in the photo, indicating presence and absence, respectively, of iron compounds in the wood. (Pictures belongs to Dr. G. Almkvist used with permission)

On the micro-level the deposits of iron compounds from the impregnation were found in and on the lumina walls of vessels and fibres. This pattern appears similar to the iron distribution found in the *Vasa* wood (Almkvist and Persson, 2011). Moreover the elemental ratio between iron and chlorine was higher in the impregnated wood, Fe:Cl> 2, compared to the original treatment solution, Fe:Cl = 0.5. Results from *Vasa* wood imply an even higher iron:chlorine ratio, which together with the data presented here indicates a much stronger adsorption of iron(II) ions to the wood than chloride ions during the impregnation (manuscript I).

3.2 Average molecular weight

The average molecular weight (AMW) distribution of holocellulose was analyzed in one iron(II) impregnated sample exposed to air for one week, sample #3, Table 2. The change in molecular weight distribution shows similarities to those earlier observed in *Vasa* wood rich in iron compounds and exposed to air, Figure 12 (Lindfors et al., 2008) and to holocellulose treated by Fenton´s reagent (Almkvist and Persson, 2008b). The similarity in the results of iron impregnated recent oak wood and dry samples from *Vasa* is striking. The results are compared to recent oak as reference sample. The decrease in degree of polymerization of holocellulose is significant and in accordance with the tensile strength results (Figure 13).

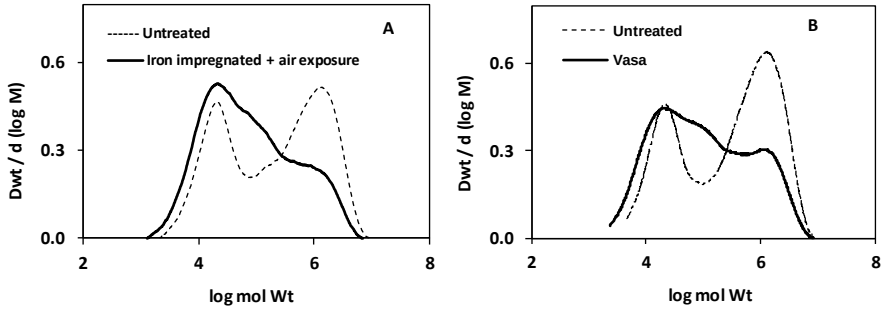

Figure 12. Average molecular weight distributions of holocellulose prepared from (A) an iron(II) impregnated sample (this report) and (B) *Vasa* sample (Almkvist and Persson, 2008b).

3.3 Mechanical properties

The relationship between stress and strain could be considered as linear in most cases (for both the reference and treated specimens), and very little indication of plasticity was seen before failure for both recent (Bjurhager, 2008) and *Vasa* oak (Bjurhager et al., 2008). Tensile strength, σ, (including statistical data), Young's modulus, E, (i.e. tensile stiffness) and strain to failure, ε, are given in Appendix I. Tensile strength, Young's modulus and strain to failure for all the untreated references are to be considered as normal in comparison to previous studies (Bjurhager, 2008). The average values are strain σ=107 (14) MPa, stiffness, *E,* 13.3 (1.9) GPa, and strain, ε, 0.89 (0.08) %, respectively (standard deviation in parenthesis). This means that the piece of oak chosen for sample preparation was representative for fresh oak wood in good condition, and that the mechanical results are applicable to recent oak in general.

It is obvious that the presence of iron(II) ions in the wood matrix at ambient conditions together with oxygen has a negative impact on the tensile strength of the wood in the axial direction (Table 2 and Figure 14). All results are relative to the twin reference wood samples which were cut adjacent to the treated ones. The statistical significance between groups of treated samples and their references was determined from a two-sided *t*-test, and the significance levels were set to P<5%, 1%, 0.5% and 0.1%.

No significant effect of wetting the samples was found, sample #2. Oxygen alone on dry references had no significant effect on the tensile strength, not even after one year in 100% oxygen, while samples treated with iron showed reduced tensile strength after exposure to oxygen or air

already after one week. Samples impregnated with iron(II) and subsequent exposure to pure nitrogen (#8) displayed no significant change of tensile strength. The largest change, a 50% decrease of the wood tensile strength, was observed after one year in pure oxygen while samples left in atmospheric air and at ambient temperature and pressure resulted in a somewhat lower reduction, 35%. Wood samples pre-conditioned in nitrogen before exposure to air or oxygen, samples #7 and 9-11, displayed a lower reduction of the tensile strength compared to the series that were directly exposed from wet condition to air or oxygen environment. This is more obvious when comparing samples exposed to air for comparable time, samples #4 and #10, which has a tensile strength reduction of 27% and 17%, respectively. This shows that wood is more vulnerable toward oxygen when it is in wet condition and migration of ions inside the pores is promoted. The latter observation indicates that when *Vasa* was salvaged, during the first week/month thereafter, the deterioration of the wood most probably has been more intense than during later periods.

Table 2. Results from the tensile tension measurements on samples with different treatments and exposure to oxygen. Relative changes in treatment of #1-13 are compared to untreated references. In treatment #14-16 the changes are relative to references treated with iron(II) chloride

		Exposure time				
#	Pre-Treatment	N_2	Air	O_2	Relative change of TS (%)	Student's t-test
1	-	-	-	year	-	NO
2	Water	-	Week	-	-1	NO
3	$FeCl_2$ (aq)	-	Week	-	-18	< 1%
4	$FeCl_2$ (aq)	-	Month	-	-27	< 0.1%
5	$FeCl_2$ (aq)	-	-	Week	-19	NO
6	$FeCl_2$ (aq)	-	-	Month	-30	< 5%
7	$FeCl_2$ (aq)	Week	-	Year	-50	< 0.1%
8	$FeCl_2$ (aq)	Week	-	-	-7	NO
9	$FeCl_2$ (aq)	Week	Week	-	-6	NO
10	$FeCl_2$ (aq)	Week	Month	-	-17	< 0.1%
11	$FeCl_2$ (aq)	Week	Year	-	-35	< 0.1%
12	$FeCl_2$ (aq) RH98%	-	Month	-	-18	< 0.1%
13	Solvent-treated + $FeCl_2$ (aq)	-	Month	-	-14	< 5%
References treated with iron.						
14	pH adjusted* + $FeCl_2$ (aq)		Month	-	8[Ŧ]	NO
15	Cysteine*+ $FeCl_2$ (aq)		Month	-	2[Ŧ]	NO
16	$FeCl_2$ (aq) + PEG 600*		Month	-	29[Ŧ]	< 0.1%

*The references are treated with $FeCl_2$(aq)

[Ŧ]No increase in strength shows the inhibition grade.

The sample group treated with cysteine or acetate, samples #14 and #15, displayed no significant change in tensile strength compared to their references.

Wood samples treated with additional PEG 600, sample #16, displayed a large inhibition effect compared to groups treated with only iron(II). These samples kept their strength, while references belonging to this group lost mechanical strength up to 29 %. Due to the viscosity of the PEG solution the impregnation of iron into the wood was performed before the addition of PEG. This result is very important due to the vast use of PEG on the surface of the wood of *Vasa* as a protective agent regarding the catalytic reaction of iron(II). The poor diffusion of PEG into the wood is an

alarming sign. The surface may be protected even if the concentration of oxygen is much higher, whereas deterioration in deeper parts of the wood could be fast when oxygen is available. More studies of oxygen diffusion into the *Vasa* wood are needed. The chemical deterioration processes are less extensive at RH 98% than at RH 55%, the humidity in the museum hall. The reduction in strength of wood samples kept at RH 98% gave relative tensile strength of 18 % reduction while the samples at RH 55 % during the same time of exposure of air gave a reduction of relative tensile strength of 27 %. It is shown that the generation of low molecular acids in samples kept in RH 98% increased significantly relative to the reference, Table 4. The reduction of tensile strength under humid conditions may therefore be caused mainly by acid hydrolysis rather than iron(II) catalysis for the latter samples.

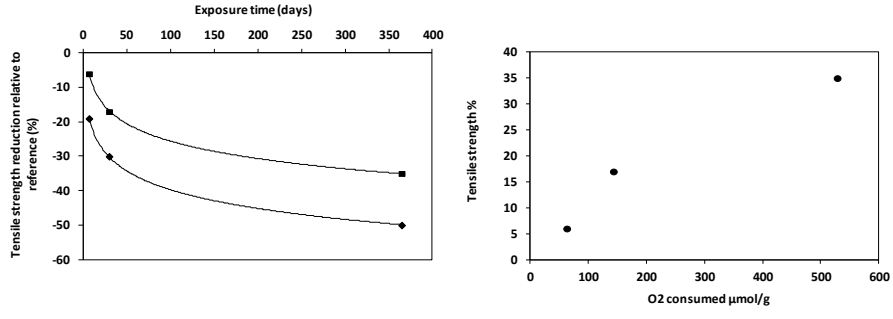

Figure 13. The tensile strength reduction in iron(II) impregnated wood samples as a function of time exposed to pure oxygen (◆) and air (■) for one week, one month and one year (left). The relation between the absolute value of tensile strength and consumption of oxygen after one week, one month and one year is slightly linear (right).

Group #13, the samples with low or no extractives, displayed a reduction of tensile strength of 14 %. This result indicates that wood extractives which may form complexes with iron ions, affect the chemical properties of the iron ions, and thereby also the reactions between iron and oxygen. Iron tends to form complexes with wood extractives, especially with tannins (Jaen et al., 1999, Engle-Stone et al., 2005). According to Theise et al. (1974), an iron(II) tannate complex has an inhibitory effect on oxidation of iron(II) to iron(III). The tensile strength results of samples with extractives show that these are more affected by iron(II) than those with a low amount of extractives. Iron(II) may oxidize to iron(III) more rapidly when the extractives are absent and thereby the catalytic reactions of wood are inhibited.

3.4 Oxygen consumption

3.4.1 Solid piece

The results show that the consumption of oxygen was highest in an the initial stage and then declined with time, Figure 14. After one year, the consumption of oxygen was still ongoing although the rate had declined compared to the initial measuring period of measuring. More than 500 µmole O_2/g wood was consumed after one year. One oxygen molecule may oxidize four iron(II) ions to iron(III) which gives the possibility to compare the amount of iron(II) absorbed and total amount of oxygen consumed. This is in accordance to the amount of total amount of iron(II) absorbed in the wood which is approximately 1200 µmole/g wood, thus a iron(II):O_2 ratio of 25%.

The transport of oxygen into the wood matrix is diffusion controlled. This is shown by the linear relation of the square root of time of measurement and oxygen consumption. The linearity and the intercept from origo describes the intraparticle diffusion seen when plotting change in oxygen concentration (in this study) against the square root of time (Ho et al., 2000). The appropriate equation (Ho et al., 2000, Cheung et al., 2007, Hameed, 2009) is

$$q_t = k_d\sqrt{t} \qquad (4)$$

there q_t is the substance which is diffusing (µmol g^{-1}) and k_d is the rate constant (µmol g^{-1} $day^{½}$). Equation (4) is related to Fick's second law, equation (5), which describes diffusion for time (t), concentration gradient (d*c*/d*x*) and distance (x) diffused in the medium (Evans and Wennerström, 1999).

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \qquad (5)$$

there d*c* is change in oxygen concentration, d*t* is change in time and *D* is the diffusion coefficient (m^2s^{-1}).

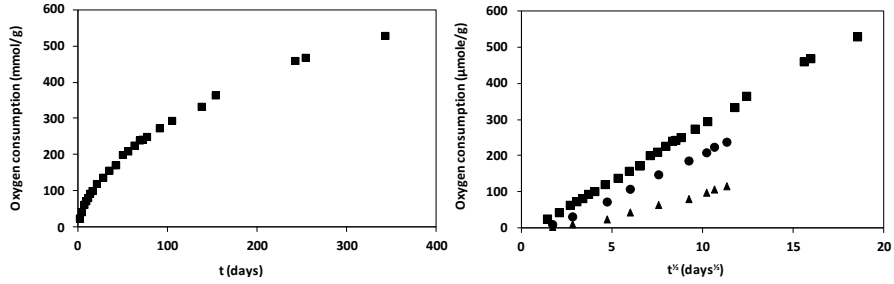

Figure 14. Accumulated oxygen consumption in iron impreganated oak wood in RH 55 % as a function of time (left) and as a function of the square root of time (right). Different levels of Fe(II) impregnation: 0.1 M (box), 0.05 M (circle) and 0.01 M (triangle).

The oak wood samples kept at different relative humidity were tested and the oxygen concentrations inside the vials were measured even though the main focus was on RH 55%. The oxygen consumption in samples treated in different relative humidity shows that the initial consumption rate was higher when the RH was kept low and the rate was inversely proportional to RH, Figure 15. The consumption declined to approximately 1.5 µmol/g/day after hundred days of exposure.

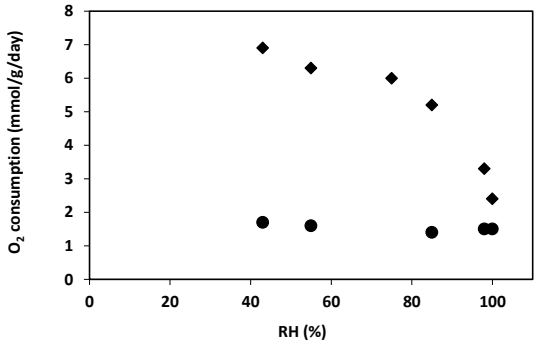

Figure 15. Oxygen consumption as a function of relative humidity for oak samples treated with 0.1 M iron(II) chloride the first week (initial ◆) and after 100 days (●).

This may explain the lower degradation of wood at RH 98% as measured by tensile strength, which decreased to 18% for samples kept at RH 98% whereas samples with the same treatment and time kept at RH 55% decreased to 27%. The relation between oxygen consumption at different RH and the reduction of tensile strength could be correlated.

Interestingly, at higher relative humidity, the emission of CO_2 increased. The molar ratio of the formed carbon dioxide to oxygen

consumed as a function of the relative humidity (Figure 16) shows that at RH 100% nearly all oxygen consumed was converted into carbon dioxide whereas at RH 43% the emitted CO_2 was negligible relative to the consumed O_2. Apparently, a high RH slows down the rapid consumption of O_2 but the relative production of CO_2 increases. Release of carbon dioxide at high RH may indicate a biological activity, which was not specifically investigated for these samples. Reference samples consumed and emitted very low amounts of oxygen and carbon dioxide, respectively.

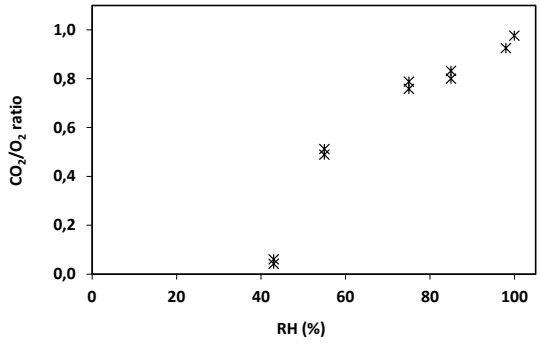

Figure 16. The ratio of produced CO_2 to consumed O_2 as a function of the relative humidity.

The high amount of water in the wood matrix at high RH may limit the oxygen accessibility. The ratio of CO_2:O_2 starts to decline at RH 75% which is an intermediate condition between wet (EMC 30%) and dry (EMC 10%) condition. It seems that different reactions take place at different RH. This is shown in Table 4 regarding the formation of low molecular acids. At high RH the amount of these acids are significantly higher than those treated at RH 55% which is the present humidity at museum hall. The effects at higher RH are relevant, since all parts of the *Vasa* hull have gradually gone through these humidity regimes during the preservation.

3.4.2 Powder samples

The oxygen consumption of the powder samples is shown in Figure 17. Although the difference between the reference samples and the treated ones is not significant, the results clearly imply that wood extractives increase the oxygen consumption and promote the oxidative reaction caused by iron and oxygen. The reference sample without any pre-treatment, impregnated in iron solution, shows the highest rate of consumption. As more wood extractives are washed away the rate of oxygen consumption declines. Samples extracted with acetone/water and

toluene/ethanol show similar consumption of oxygen, while the sample treated with 2-propanol and 1% sodium hydroxide has the lowest consumption. This may explain the result for the sample treated with solvents in Table 2, #13, where the tensile strength was not reduced as much as the reference samples with similar treatment.

The total concentration of iron in these samples was determined. The iron impregnated oak showed the highest concentration compared to the other samples with low or no extractives, Table 3. The wood susceptibility to the aqueous iron solution was lowered drastically after the first extraction step, but to some extent normalized after the second and third solvent treatments. According to Maldas et al. (Maldas and Kamdem, 1999) the hydrophobic extractives, such as waxes and long chain hydrocarbons, migrate toward the surface of the wood and reduces the ability to wet. This will decrease the accessibility of water and aqueous solutions to the wood. The hydrophobic extractives may have blocked the diffusion of iron which might explain why the amount of iron was low after the first treatment. As pointed out above, the samples further solvent treated where even the hydrophobic extractives were washed away, reached more normal diffusion conditions. Although the sample treated with acetone/water mixture contains only 25% iron compared to the untreated wood, it does not show any significant difference regarding oxygen consumption. Thus, no correlation of concentration of iron in wood and to consumed oxygen could be observed.

Table 3. The total amount of iron for oak powder with and without extractives

	$Fe_{(mg/g)}$	total O_2 $consumed_{(\mu mol/g)}$
Oak	4.5	401 (24)
Acetone/H_2O	1.1	320 (86)
Toluene/EtOH	3.3	353 (48)
2Propanol/NaOH	3.0	274 (-)*

* Parenthesis denotes the standard deviation. Last group was a double sample, hence no SD.

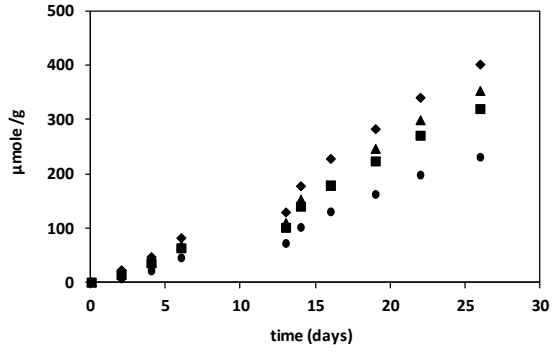

Figure 17. The cumulative consumption of oxygen from milled oak wood treated with different solvents and impregnated with iron(II) chloride. The reference oak sample (◆) with highest amount of extractives consume oxygen most. (■), (▲) and (●) denote milled oak wood treated with acetone/water 7:3; toluene/ethanol 2:1 and 2-propanol/sodium hydroxide, respectively.

3.4.3 Acids

The concentration of low molecular acids and pH was analyzed for some of the samples. The pH of the extracted aqueous solutions of ground samples was measured. For the iron impregnated and oxygen treated sample at 55% RH, a slight increase in the concentrations of acetic, formic, glycolic and oxalic acid was observed, Table 4. The concentration of oxalic acid is in the range of 0.1-0.3 mg/g wood, which is far below the levels that are found in samples from the most severely degraded sites in the *Vasa,* 2-5 mg/g wood (Almkvist and Persson, 2008a). However, a long-term exposure of samples to air at higher RH, 85% and 98%, revealed significantly elevated concentrations of oxalic acid, suggesting that the required chemical conditions for its formation are fulfilled at high RH. The water content in deeper parts of wood from *Vasa* may be enough to promote the migration of iron(II). Therefore, if water-rich regions still exist and/or if the humidity increases, the wood of Vasa may probably behave as the samples treated at high RH.

Samples treated with cysteine and PEG seems to have no effect on the concentration of acids except change in pH. Generally, the formation of acids is somewhat limited for samples treated at a relative humidity of 55%. The interaction of iron and oxygen may not produce acids at conditions where the water content is limited. The low pH for iron(II) treated samples was probably caused by generated organic acids other than oxalic. However, the presence of relatively high concentrations of oxalic acid in the wood may play an important role in the deterioration

processes. The low p*K*a value of oxalic acid lowers the pH to such extend that acid hydrolysis of polysaccharides elevates (Tanaka et al., 1994). Regarding the relation of oxalate and Fenton reaction, Tanaka et al. showed that the concentration ratio of oxalate and iron, determine if Fenton reaction is suppressed or promoted. Up to ten times higher concentration of oxalate relative to iron will encouraged Fenton reactions and suppress it when the oxalate:iron ratio is higher than that (Schmidt, 1981, Tanaka et al., 1994).

The total amount of acids from samples with low/no extractives are ca. 2.0-2.5 mg/g wood while solid samples have a range between 1.0-3.6 mg/g wood. This is in accordance with the pH values except for the sample treated with additional cysteine which has a lower pH value and low concentration of acids. Regarding samples treated in high RH, the total acid formation is 2-4 times higher than samples treated at RH 55%. The results indicate that the degradation of wood at RH 55% may be caused by a Fenton-type reaction than acid hydrolysis. The impact of hydroxyl radicals is much faster than an acidic proton attack. This is shown in Tables 2 and 4 where samples kept in high RH for one month generate more of the low molecular acids, but the tensile strength is comparable to samples treated in RH 55% exposed to oxygen for shorter time (compare sample #3 and #12, Table 2).

Table *4*. pH values and total amount of organic low molecular acids in oak wood treated and exposed to air/oxygen

				Low molecular acids (mg g-1)			
	#	Pre-treatment	pH	Acetic	Formic	Glycolic	Oxalic
Solid	1	Ref.	3.8	2.2	0.1	0.1	0.1
	3	$FeCl_2$ (aq)	2.4	3.1	0.2	0.1	0.2
	7	$FeCl_2$ (aq)	2.4	2.9	0.3	0.1	0.2
	13	$FeCl_2$ (aq)/ cysteine	2.2	0.8	0.1	0.1	0.0
	16	$FeCl_2$ (aq)/ PEG600	2.4	2.2	0.2	0.1	0.1
Powder*	RH 55%	$FeCl_2$ (aq)-ref.	3.0	1.5	0.5	0.1	0.3
		Acetone/H_2O	3.1	1.4	0.6	0.1	0.3
		Toluene/EtOH	3.0	1.5	0.5	0.1	0.2
		2Propanol/NaOH	3.2	1.1	0.6	0.1	0.2
ΔRH	RH 98 %	$FeCl_2$ (aq)	2.4	2.0	0.7	1.3	2.2
	RH 85 %	$FeCl_2$ (aq)	2.0	5.1	1.2	1.0	2.9
	RH 55 %	$FeCl_2$ (aq)	2.4	2.9	0.3	0.1	0.2
	RH 55 %	Water	3.6	0.3	< 0.1	< 0.1	< 0.1

Same numbering as in Table 2

4 Conclusion

This study has shown that the tensile strength of oak wood is significantly reduced when iron(II) and oxygen are present. The observed average molecular weight of recent oak treated with iron(II) and exposed to oxygen is similar to the result observed for wood from *Vasa*. This shows that deterioration of wood in the *Vasa* may have been affected in a similar way, i.e. interaction of iron and oxygen. The results show that the rate of reactions involving deterioration of wood is higher at the initial stage. The high rate indicates that the oxygen concentration in the wood may be the limiting factor which determines the extent of depolymerization of cellulose. A combination of results from measurements of tensile strength and oxygen consumption within the same time frame gave an almost linear relation between these two parameters.

The amount of low molecular acids found in the *Vasa* is more similar to those samples treated in high relative humidity relative to the present museum climate. This indicates that the acids were probably formed during times with high humidity and no or poor climate control.

The chemical formation of oxalic acid and carbon dioxide at high RH urge for further investigation. The degradation in terms of depolymerization is maybe not primarily connected to the formation of acids. Both depolymerization and acid formation may be a result of oxidative processes, albeit with different time dependence or different courses of reaction. The changes in oxygen and carbon dioxide flux observed seem to depend on the availability of water in an iron(II) impregnated context, which may contribute to such a model describing the reactions in the *Vasa* wood. By using the parameters from all the involved substances and replicate the condition in a mathematical model e.g. a

statistical model, it may able to make to a good prediction of the kind of processes ongoing.

To confirm the evidence of hydroxyl radicals and peroxides further investigations are needed. Electron paramagnetic resonance, EPR, is one of the techniques which could be applied to both simulated wood samples as in this study and to wood from *Vasa*. Further investigation is also needed regarding the rate of diffusion of oxygen into the wood. As it is confirmed in this study that the rate of deterioration of wood rich in iron(II) depends on both concentration and time of exposure of oxygen, it is important to create a model for prediction of the diffusion of oxygen.

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Appendix

Tensile strength, Young's modulus and Strain to fracture

#	Pre-Treatment	Number of samples	N_2	Air	O_2	Tensile strength σ (stdev) [Mpa]	Tensile stifness Young's mod. E (stdev) [Gpa]	Strain to fracture ε (stdev) [%]
1	-	6	-	-	Week	97 (27)	11.6 (3.5)	1.00 (0.15)
	reference	6	-	-	Week	95 (29)	11.2 (3.3)	0.90 (0.07)
	-	7	-	-	month	113 (13)	14.5 (2.2)	0.74 (0.08)
	reference	6	-	-	month	112 (9)	13.9 (1.2)	0.79 (0.08)
	-	7	-	-	year	100 (8)	14.0 (1.3)	0.74 (0.05)
	reference	6	-	-	year	107 (14)	13.6 (1.5)	0.79 (0.08)
2	Water	7	-	Week	-	127 (19)	13.4 (1.5)	1.01 (0.16)
	reference	6	-	Week	-	128 (27)	13.0 (2.0)	0.95 (0.10)
3	$FeCl_2$ (aq)	24	-	Week	-	97 (19)	13.1 (2.1)	0.83 (0.11)
	Water (ref.)	16		Week	-	118 (29)	13.6 (2.4)	0.99 (0.16)
4	$FeCl_2$ (aq)	24	-	Month	-	93 (16)	12.7 (2.6)	0.78 (0.09)
	Water (ref.)	16	-	Month	-	127 (23)	14.2 (3.2)	1.00 (0.14)
5	FeCl2 (aq)	7	-	-	Week	76 (20)	11.5 (3.8)	0.67 (0.10)
	Water (ref.)	6	-	-	Week	94 (16)	11.8 (2.0)	0.84 (0.08)

Tensile strength, Young's modulus and Strain to fracture

#	Pre-Treatment	Number of samples	N_2	Air	O_2	Tensile strength σ (stdev) [Mpa]	Tensile stifness Young's mod. E (stdev) [Gpa]	Strain to fracture ε (stdev) [%]
6	$FeCl_2$ (aq)	7	-	-	Month	57 (12)	11.2 (2.6)	0.61 (0.07)
	Water (ref.)	6	-	-	Month	81 (17)	9.6 (2.4)	0.89 (0.13)
7	$FeCl_2$ (aq)	7	Week	-	Year	60 (6)	14.9 (1.5)	0.44 (0.08)
	Water (ref.)	6	Week	-	Year	118 (20)	15.4 (3.0)	0.80 (0.11)
8	$FeCl_2$ (aq)	7	Week	-	-	114 (16)	13.8 (0.7)	0.83 (0.07)
	Water (ref.)	6	Week	-	-	122 (15)	14.5 (1.6)	0.86 (0.07)
9	$FeCl_2$ (aq)	7	Week	Week	-	87 (16)	11.5 (2.0)	0.73 (0.09)
	Water (ref.)	6	Week	Week	-	93 (25)	11.8 (3.2)	0.83 (0.13)
10	$FeCl_2$ (aq)	7	Week	Month	-	96 (8)	16.1 (1.3)	0.65 (0.07)
	Water (ref.)	6	Week	Month	-	115 (5)	15.6 (1.3)	0.80 (0.11)
11	$FeCl_2$ (aq)	7	Week	Year	-	83 (13)	14.2 (2.4)	0.48 (0.10)
	Water (ref.)	6	Week	Year	-	128 (12)	16.8 (2.0)	0.92 (0.16)
12	$FeCl_2$ (aq); RH 98%	32	-	Month	-	86 (13)	11.3 (2.3)	0.87 (0.13)
	Water (ref.); RH 98%	8	-	Month	-	106 (13)	12.3 (2.7)	1.02 (0.09)

Tensile strength, Young's modulus and Strain to fracture

#	Pre-Treatment	Number of samples	N_2	Air	O_2	Tensile strength σ (stdev) [Mpa]	Tensile stifness Young's mod. E (stdev) [Gpa]	Strain to fracture ε (stdev) [%]
13	Solvent-treated + FeCl2 (aq)	25	-	Month	-	101 (18)	12.5 (3.5)	0.80 (0.11)
	Water (ref.)	15	-	Month	-	118 (31)	12.6 (1.6)	1.00 (0.22)
14	pH adjusted	12	-	Month	-	85 (12)	12.0 (4.0)	0.70 (0.13)
	$FeCl_2$ (aq) (ref.)	8	-	Month	-	79 (9)	10.2 (4.1)	0.63 (0.06)
15	Cysteine + $FeCl_2$ (aq)	24	-	Month	-	85 (22)	13.3 (2.1)	0.67 (0.15)
	$FeCl_2$ (aq) (ref.)	17	-	Month	-	84 (26)	13.2 (3.2)	0.63 (0.16)
16	$FeCl_2$ (aq) + PEG 600	24	-	Month	-	92 (16)	11.5 (1.8)	0.87 (0.13)
	$FeCl_2$ (aq) (ref.)	16	-	Month	-	71 (17)	11.8 (1.8)	0.61 (0.13)